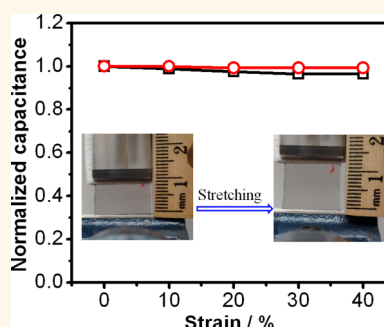


Transparent and Stretchable High-Performance Supercapacitors Based on Wrinkled Graphene Electrodes

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ABSTRACT Transparent and/or stretchable energy storage devices have attracted intense attention due to their unique optical and/or mechanical properties as well as their intrinsic energy storage function. However, it remains a great challenge to integrate transparent and stretchable properties into an energy storage device because the currently developed electrodes are either transparent or stretchable, but not both. Herein, we report a simple method to fabricate wrinkled graphene with high stretchability and transparency. The resultant wrinkled graphene sheets were used as both current collector and electrode materials to develop transparent and stretchable supercapacitors, which showed a high transparency (57% at 550 nm) and can be stretched up to 40% strain without obvious performance change over hundreds of stretching cycles.



KEYWORDS: graphene · wrinkled electrode · supercapacitor · transparency · stretchability

Stretchable electronics with highly stable performance under strains have recently attracted a great deal of interest.^{1–7} In this regard, various stretchable electronic devices, including solar cells,² light-emitting diodes,³ batteries,⁴ and textile supercapacitors,⁷ have been developed to retain their functions even when they were under large strains (up to 40%). Along this line, some transparent solar cells,^{8,9} batteries,¹⁰ and supercapacitors^{11,12} have also been developed. However, most of the currently developed electrodes and the associated supercapacitor cells cannot be both transparent and stretchable.^{13–18} It is highly desirable to integrate the stretchable and transparent characteristics into a single device for some specialty applications, such as aesthetically pleasing wearable electronics and integrated energy conversion and storage systems.¹⁹ However, it is still a big challenge to construct both stretchable and transparent electronic devices (*e.g.*, supercapacitors) because most of the existing electrodes are neither stretchable nor transparent (*e.g.*, metal electrodes) with some of them either stretchable of a low transmittance (*e.g.*, conducting polymers)

or transparent of a low stretchability (*e.g.*, ITO, other metal oxides). If successfully developed, however, the stretchable and transparent electronics should open up new possibilities for multifunctional applications of electronics in various energy, biomedical, and wearable optoelectronic systems.

In this study, we have synthesized highly transparent (up to 60% at 550 nm) and stretchable multilayer graphene sheets with a wrinkled structure, which, after being transferred onto a polydimethylsiloxane (PDMS) substrate, were used as both the current collector and active electrodes for the development of high-performance transparent (57%) and stretchable (up to 40% strain) all-solid supercapacitors with an excellent stability even over hundreds of stretching cycles.

In spite of its excellent electrical, optical, and mechanical properties, graphene has rarely been discussed in the literature for applications as stretchable electrodes since stretching often reduces its electrical conductivity dramatically. For instance, it was found that the electrical resistance of a graphene sheet transferred onto a prestrained

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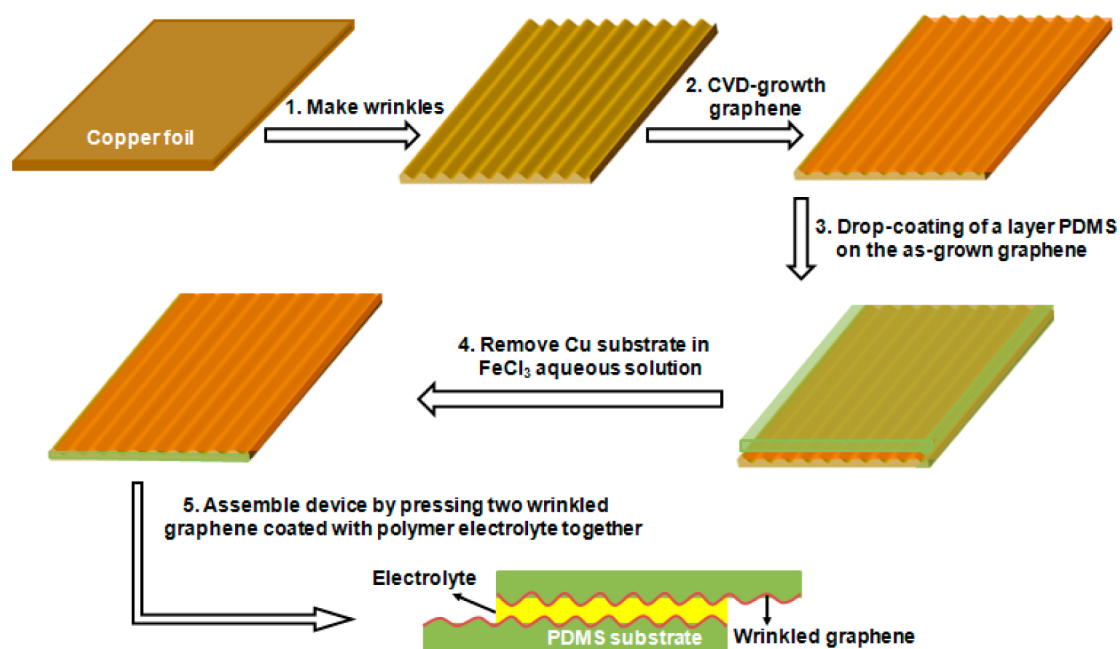


Figure 1. Schematic representation of the procedures for producing wrinkled graphene sheets for the fabrication of transparent and stretchable supercapacitors.

elastic substrate (e.g., polydimethylsiloxane) increased by more than 1 order upon stretching to 25% strain.²⁰ Besides, the process to transfer a large-area ($>2 \times 2 \text{ cm}^2$) graphene film from the growth substrate to a prestrained elastic substrate (e.g., PDMS) often causes serious cracking or breakage of the graphene sheet.^{20–22} As such, very limited effort has been made to develop transparent and stretchable graphene electrodes, which is very difficult, if not impossible. Therefore, recent research on the development of stretchable electrodes extended to the fabrication of conductive composites with carbon nanotubes or metal nanowires on elastic substrates of wrinkled (or buckled) structures, which can be easily stretched.^{1,23–26} However, most of these electrodes cannot be used in transparent electronics because of the poor transparency intrinsically associated with carbon nanotubes and metal nanowires.

Owing to its high conductivity and excellent transparency (transmittance up to 95% for 2 nm thick film),^{27–32} the one atom thick graphene sheet provides an ideal electrode material for high-performance stretchable and transparent optoelectronics. In order to realize this possibility, we synthesized the first wrinkled graphene sheet of a large area ($2 \times 4 \text{ cm}^2$) by chemical vapor deposition (CVD) of methane (flow rate of 5 sccm) with the carrier gas of argon and hydrogen (flow rate of 400 sccm/60 sccm) under 1000 °C. The wrinkled graphene sheet was then transferred with its structural integrity onto a PDMS substrate to exhibit high transparency (50–60% at 550 nm) and stretchability. We found that the resistance of the newly synthesized wrinkled graphene sheet composited with polyvinyl alcohol (PVA) to be used as a protecting layer and/or electrolyte matrix

(*vide infra*) increased by only 170% even when it was stretched up to 40% strain, showing a much better stretchability than the planar graphene sheet transferred on the prestrained elastic substrate reported by others (10 times increase in resistance up to 25% strain).²⁰

RESULTS AND DISCUSSION

Figure 1 schematically shows the procedures for the synthesis of the wrinkled graphene sheets and the subsequent fabrication of the graphene-based transparent and stretchable supercapacitors. As can be seen in Figure 1, a tweezer with an appropriate wrinkled structure (Supporting Information Figure S1) was used to produce a wrinkled copper (Cu) foil (step 1 of Figure 1) by sliding it over the Cu foil (Figure S1). The resultant wrinkled Cu foil was then used as the substrate for the graphene growth by CVD of methane as the carbon source under the mixture carrier gas of argon and hydrogen at 1000 °C in a tube furnace (step 2 of Figure 1), followed by coating a thin ($\sim 0.5 \text{ nm}$) layer of PDMS onto the top surface of the as-prepared graphene sheet and thermally solidified at 75 °C for 1 h (step 3 of Figure 1). By removing the Cu substrate in an aqueous solution of 1 M FeCl_3 ,³⁰ a large piece of stretchable wrinkled graphene sheet ($2 \times 4 \text{ cm}^2$) on PDMS was obtained (step 4 of Figure 1). Finally, the transparent and stretchable all-solid-state supercapacitors were assembled by pressing two of the PDMS-supported graphene electrodes together with a transparent layer of polymer electrolyte (a solution of PVA and H_3PO_4 in water) between as both the electrolyte and separator (step 5 of Figure 1).

Figures 2a,b show digital photographs of the copper foil, before (a) and after (b) the wrinkle formation, used for the graphene deposition. Scanning electron microscopic (SEM) imaging was performed after transferring

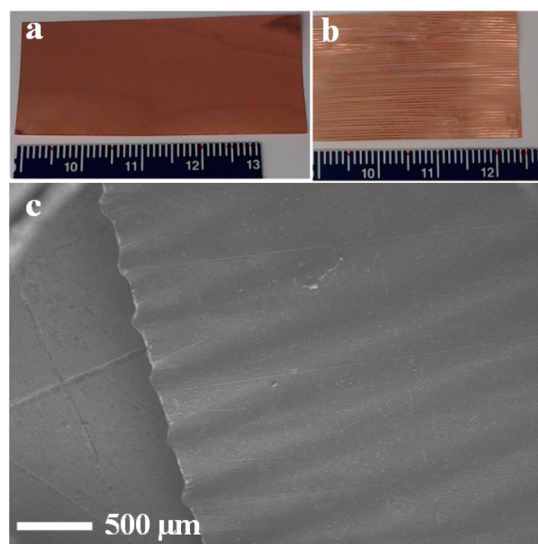


Figure 2. Morphology and structure of the wrinkled graphene sheets. (a,b) Digital photographic images of the copper foil before (a) and after (b) the wrinkle formation. (c) Typical SEM image of the wrinkled graphene sheet on the PDMS substrate from the top view.

the resultant wrinkled graphene sheet onto the PDMS substrate. As can be seen in Figure 2c, the wrinkled graphene sheet showed a wave-like surface structure with an interwrinkle distance of about 400 μm . Depending on the graphene growth durations (Figure S2), the PDMS-supported wrinkled graphene sheets exhibited an optical transmittance in the range of 50 to 60% (at 550 nm, 94% transmittance for the 0.5 mm thick PDMS substrate), which are comparable to the multilayered planar graphene sheet (53–62%) prepared under the same condition. The wrinkled graphene sheets showed transparency slightly lower than that of the planar graphene sheets synthesized at the same condition (Figure S2), which can be attributed to the light diffuse reflectance and light-scattering effects associated with the wavy surface. Given that the transmittance reduction by a single graphene layer is about 2.3%,³³ the observed 50–60% transmittance indicated that the average number of graphene layers is about 10 (growth for 1 min) to 20 (growth for 3 min).

Figure 3a shows Raman spectra of the wrinkled graphene sheets prepared by CVD for different deposition times, which, as expected, shows a G peak at $\sim 1585\text{ cm}^{-1}$ and 2D peak at $\sim 2710\text{ cm}^{-1}$ for the graphitic carbon. The I_D/I_G ratio (the peak intensity ratio of the D peak versus G peak) reduced from 0.30 to 0.23, together with a decrease in the I_{2D}/I_G ratio from

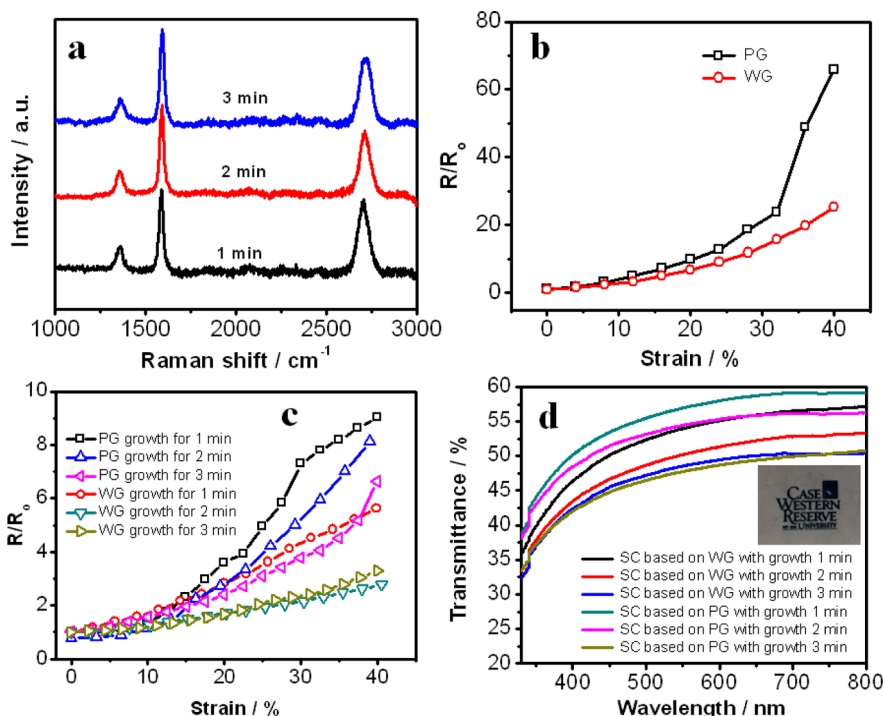


Figure 3. Characterization of the planar and wrinkled graphene sheets (designated as PG and WG, respectively). (a) Raman spectra of the WG sheets with different growth times. (b) Dependency of resistance of the PG and WG sheets (CVD deposition for 3 min) on the tensile strain. (c) Dependency of resistance of the PVA-coated planar and wrinkled graphene sheets with different CVD deposition times on the tensile strain. (d) Transmittance of supercapacitors (SC) based on the PG and WG with different CVD deposition times. The inset of (d) shows a digital photograph of a supercapacitor device on a piece of paper printed with Case logo (with permission from Case Western Reserve University), demonstrating the transparent nature of the supercapacitor device.

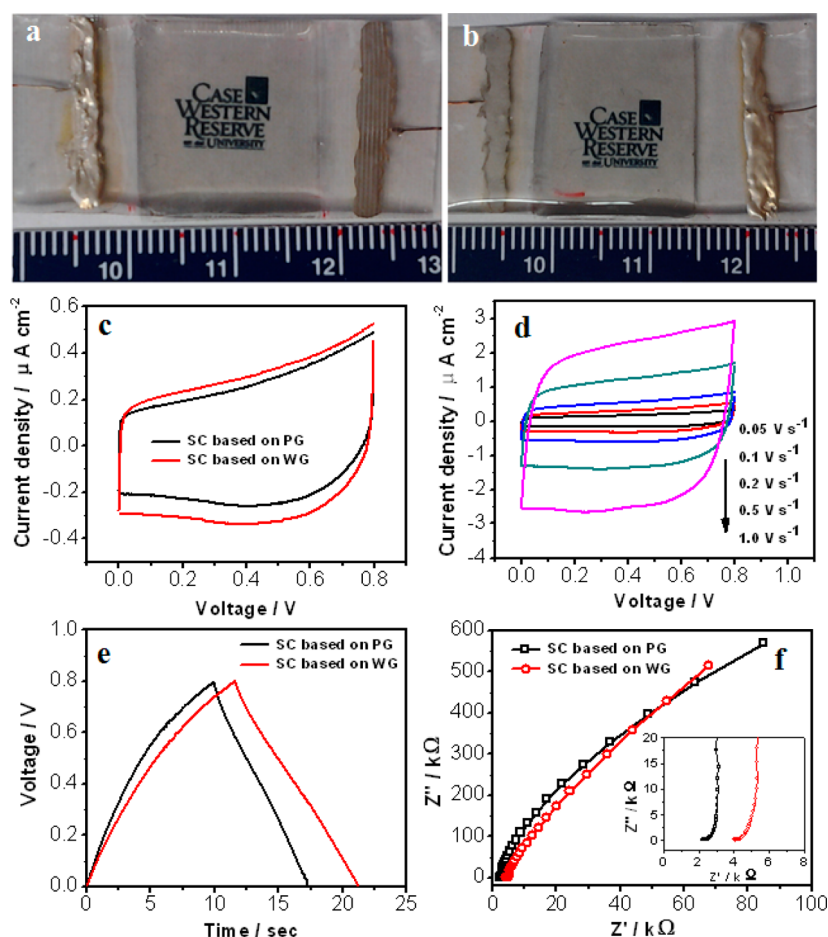


Figure 4. Transparent supercapacitors based on PG and WG with the growth time of 2 min. Digital photographic images of the supercapacitors based on the (a) WG and (b) PG (the logo was used with permission from Case Western Reserve University). (c) CV curves of the supercapacitors using the PG and WG at the scan rate of 0.1 V s⁻¹. (d) CV curves of the supercapacitors based on the WG at different scan rates. (e) Galvanostatic charging–discharging curves of the supercapacitors at a constant current of 0.8 μA. (f) Nyquist plots of the supercapacitors with a frequency range from 10⁻² to 10⁵ Hz.

0.88 to 0.68 as the growth time increased from 1 to 3 min. This indicates, once again, the multilayered nature of the wrinkled graphene sheets with the layer number increased by increasing the growth time.^{34–36} Both the planar and wrinkled graphene sheets synthesized under the same conditions showed a comparable electrical resistance (Figure S3), which decreased from 1250 to 600 Ω cm⁻¹ with increasing growth time from 1 to 3 min due to the increased graphene layer number.

To evaluate the stretchability, we performed the tensile strain measurements for both the planar and wrinkled graphene sheets. Due to the inevitable stretching-induced fracture of the graphene sheet, the resistance of the wrinkled graphene sheet increased by about 25 times when it was stretched up to 40% strain, whereas the corresponding value for the planar graphene sheet is more than 60-fold (Figure 3b), showing a much better stretchability for the wrinkled graphene sheet. The strong resistance–strain dependence observed for the graphene sheet could be useful for the development of graphene-based strain sensors³⁷ but not the stable stretchable electronic

devices to be developed in this work. Therefore, a layer of PVA (~5 μm thick) was coated onto the surface of both the planar and wrinkled graphene sheets to prevent/minimize the stretching-induced crack of the graphene sheet and hence improved stretchability. Indeed, the stretchability of both the planar and wrinkled graphene sheets was improved significantly by PVA coating, which was used as both the protecting layer and electrolyte matrix (*vide infra*). Compared with the PVA-coated planar graphene sheet, the PVA-coated wrinkled graphene sheet exhibited an even better stretchability. As shown in Figure 3c, the resistance of the PVA-coated wrinkled graphene sheet (prepared by CVD for 3 min deposition) increased by less than 2-fold when it was stretched up to a strain of 40%, while the resistance of the corresponding PVA-coated planar graphene sheet increased by about 6-fold at the same strain (Figure 3c). Figure 3c also shows that both the planar and wrinkled graphene sheets prepared by CVD for 3 min deposition possess better stretchabilities, at almost any constant strains covered by this study, than their counterparts produced

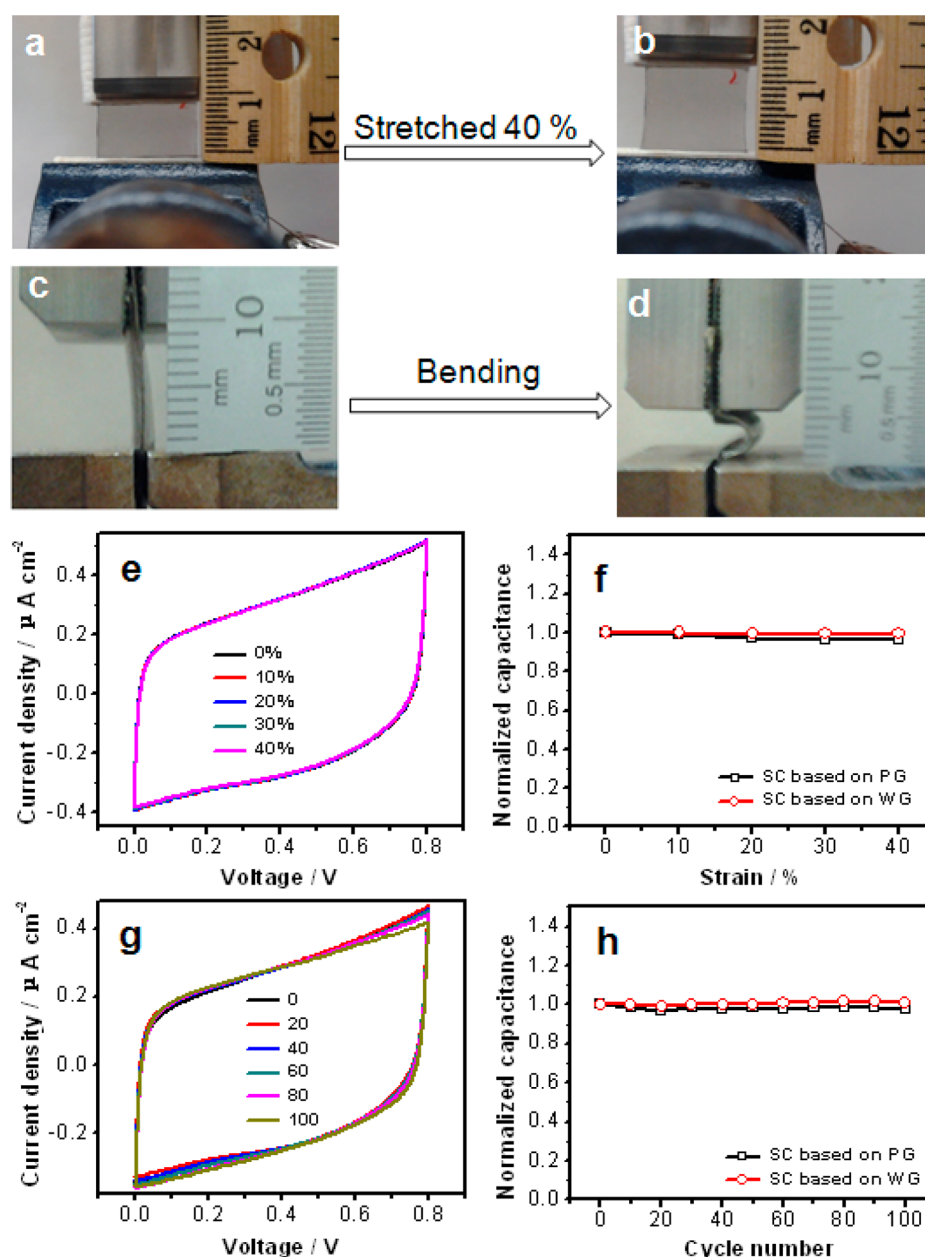


Figure 5. Stretchability and flexibility of the transparent supercapacitors based on the wrinkled graphene sheets. (a,b) Digital photographs of the supercapacitors before (a) and after (b) being stretched up to 40% strain. (c,d) Digital photographs of the supercapacitors before (c) and after (d) being bent. (e) CV curves of the supercapacitor with different tensile strains at a scan rate of 0.1 V s^{-1} (note that other CV curves were overlapped by the two colored ones shown in the figure). (f) Normalized surface-specific capacitance of the supercapacitors based on either the planar or wrinkled graphene sheet as a function of strain. (g) CV curves of the supercapacitor with different stretching cycles at a scan rate of 0.1 V s^{-1} . (h) Normalized surface-specific capacitance of two types of supercapacitors based on either the planar or wrinkled graphene sheet as a function of stretching cycles.

by CVD under the same conditions but with a shorter deposition time (e.g., 1 or 2 min). Although the more layered graphene sheets showed a better stretchability, the increase in layer number reduced the transmittance. Therefore, there should be a delicate balance between the stretchability and transparency for the graphene sheets to be used in the high-performance stretchable and transparent supercapacitors being developed. The high transmittance of the resultant supercapacitors is evident in Figure 3d, which shows

optical transmittances in the range of 48 to 57% depending on the growth time (i.e., the layer number) of the graphene sheets.

Figures 4a,b show digital photographs of the typical assembled supercapacitors based on the wrinkled and planar graphene sheets, respectively, that both exhibited a good transparency. Figure 4c,d reproduces CV curves from the supercapacitors based on both the planar and wrinkled graphene sheets, showing an excellent capacitive behavior with nearly rectangular

shapes even at a high scan rate of 1.0 V s^{-1} (Figure 4d and S4). Galvanostatic charge/discharge curves of these transparent supercapacitors given in Figure 4e show the typical triangular shape, indicating once again nearly ideal capacitive behaviors. The specific capacitance can be calculated using the equation of $C_{\text{sp}} = 2I/\Delta t/S\Delta V$, where I is the applied current, S is the area of the active electrode in supercapacitor, Δt is the discharging time, and ΔV is the voltage window.³⁸ The surface-specific capacitances thus calculated for the supercapacitors based on the planar and wrinkled graphene sheets are 4.9 and $5.8 \mu\text{F cm}^{-2}$, respectively, while the corresponding mass-specific capacitances are 6.4 and 7.6 F g^{-1} . Figure 4f shows the Nyquist plots recorded in a frequency range from 10^{-2} to 10^5 Hz . The vertical shape at low frequencies indicated a pure capacitive behavior.³⁸ The series resistances of the supercapacitors based on the wrinkled and planar graphene sheets are 2.2 and $4.0 \text{ k}\Omega$, respectively (inset in Figure 4f). Figure S5 shows the electrochemical properties of the transparent supercapacitors based on the wrinkled graphene sheets with different CVD deposition times of 1, 2, and 3 min. As can be seen, all of them exhibited a reasonably good electrochemical performance with a similar specific capacitance of about $6.0 \mu\text{F cm}^{-2}$, a value which is similar to the specific capacitance of the $3100 \text{ m}^2/\text{g}$ surface area activated graphene.³⁹ Compared to those supercapacitors based on randomly assembled graphene electrodes with porous structures or CVD-grown graphene electrodes with sputter-coated gold current collector,^{40,41} the horizontally stacked graphene sheets assembled in our supercapacitors (with no metal current collector) have a relatively low specific surface area. Therefore, there is considerable room for further improving the performance of our supercapacitors by optimizing graphene electrodes.

We further investigated the stretchability of these transparent supercapacitors by measuring their electrochemical properties (CV and galvanostatic charging–discharging) as the devices were stretched to different strains. Figures 5a,b show digital photographs of the supercapacitors fixed on a mechanically stretching machine (MV220 motorized test stand, DS2-11 digital force gauge; IMADA, Inc.) before and after being stretched up to 40% strain. The effect of bending on the electrochemical performance of these supercapacitors was also investigated (Figures 5c,d). For supercapacitors based on both the planar and wrinkled

graphene sheets (here, graphene sheets with a growth time of 2 min were investigated), their CVs and charging–discharging performance (Figure 5e and Figures S6 and S7) as well as their specific capacitance (Figure 5f) were almost unchanged when they were stretched up to 40% strain. Furthermore, these transparent and stretchable supercapacitors also showed an outstanding stability as their CVs and capacitances did not vary over hundreds of cycles of stretching up to 40% strain (Figures 5g,h). Such a stable performance was also seen when these supercapacitors were bent instead of being stretched. As shown in Figure S8, both the CV curves and charging–discharging characteristics remained almost unchanged when the supercapacitors were bent to a large bending radius (Figures 5c,d). These results clearly indicate that the newly developed transparent supercapacitors are highly stretchable and stable.

CONCLUSIONS

In summary, we have successfully fabricated multilayered graphene sheets with a well-wrinkled structure, high transparency (up to 60% at 550 nm), and good stretchability (up to 40% strain) in terms of both the mechanical and electrical properties. After being transferred on PDMS substrates, the PDMS-supported graphene sheets were used as both the current collector and electrodes, sandwiched with a layer of polymer gel (PVA/ $\text{H}_3\text{PO}_4/\text{H}_2\text{O}$) as the solid electrolyte and separator, to fabricate transparent (57%) and stretchable all-solid supercapacitors. The newly developed transparent supercapacitors can be stretched up to 40% strain and over hundreds of stretching cycles without obvious performance change. The measured specific capacitances (e.g., surface-specific capacitance of about $5.8 \mu\text{F cm}^{-2}$ and mass-specific capacitance of 7.6 F g^{-1}) of these supercapacitors are similar to the reported specific capacitance for the $3100 \text{ m}^2/\text{g}$ surface area activated graphene.³⁹ Due to the low specific surface area of the horizontally stacked graphene sheets with no metal current collector in our supercapacitors, there is still considerable room for future improvement in device performance through optimization of the electrode/device structure. This study provides a novel strategy to develop highly transparent and stretchable all-solid supercapacitors useful for a large variety of potential applications, ranging from portable energy sources for flexible electronics to energy storage components in various stretchable integrated systems.

EXPERIMENTAL SECTION

The wrinkled copper foil was made by extruding the planar copper foil ($25 \mu\text{m}$ thick, Alfa Aesar) using tweezers with the wrinkled structure (Figure S1). Graphene sheets were grown for different times on the wrinkled and planar copper foil ($2 \times 4 \text{ cm}^2$) by CVD of methane (flow rate of 5 sccm) as the carbon source and a mixture of argon and hydrogen (flow rate

of 400 sccm/60 sccm) as the carrier gas at 1000°C . To transfer the graphene sheet onto a PDMS substrate, the mixture of the “base” and the “curing agent” at a ratio of 10:1 (Sylgard 184, Dow Corning) was poured onto the copper foil covered with the as-grown graphene sheet, followed by thermal cure at 75°C for 1 h. Graphene sheet on the PDMS was then produced after the copper was dissolved in FeCl_3 aqueous solution (1 M).

The PDMS-supported graphene sheet was cut into smaller pieces with suitable shapes and sizes. A gel solution containing PVA powder (1.0 g) and H_3PO_4 (1.0 g) in water (10.0 mL) was used as the electrolyte. The gel electrolyte was coated over most (70% length) of the graphene sheets and dried in air at room temperature for several hours. Then, two such electrolyte-coated graphene electrodes were assembled into a supercapacitor by pressing them together. Finally, a copper wire was connected to the part of the graphene sheet that was not coated by electrolyte using silver paste for the device performance characterization in a two-electrode configuration.

The structure of the graphene sheet was characterized by SEM (JEOL JSM-6510LV/LGS operated at 20 kV). UV/vis transmittance was measured with a Shimadzu UV1800 spectrometer, and Raman spectra were recorded on a Renishaw Raman spectrometer equipped with 514 nm laser. Electrochemical measurements were performed on an electrochemical working station (CHI 760C, USA). The graphene sheet or supercapacitor was fixed on a mechanical test machine (MV220 motorized test stand, DS2-11 digital force gauge; IMADA, Inc.), and the resistance and the electrochemical performance were measured under stretching and bending, respectively.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Transparent properties and electrical properties of planar and wrinkled graphene sheets. Electrochemical performance and stretchabilities of the transparent supercapacitors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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